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(54) СПОСОБ ПОЛУЧЕНИЯ БИС-(ПЕРФТОРАЛКИЛ)- ФОСФИНОВЫХ КИСЛОТ

1

Изобретение относится к новому способу получения бис-(перфторалкил)-фосфиновых кислот, которые могут найти применение в синтезе комплексообразователей, инсектицидов и поверхностно-активных веществ.

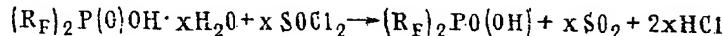
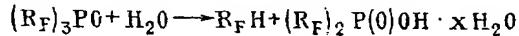
Известен способ получения бис-(трифторметил)- и бис-(перфторпропил)-фосфиновой кислот гидролизом трис-(перфторалкил)-фосфиноксидов в избытке воды при комнатной температуре в течение 24 час с идентификацией кислоты в виде серебряной соли.

2

Однако известный способ многостадиен, сложен и дорог.

Цель изобретения — упрощение способа достигается тем, что процесс проводят при 5 100—150°С с последующим выделением целевого продукта кипячением полученной реакционной смеси с хлористым тионилом. После отгонки избытка хлористого тионила индивидуальные кислоты выделяют перегонкой в 10 вакууме. Выход 70—90%.

Процесс протекает по схеме:

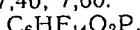


где R_F — перфторалкил.

Пример 1. В колбу на 50 мл, снабженную обратным холодильником и счетчиком пузырьков газа, помещают 20,3 г (0,037 г-моль) трис-(перфторпропил)-фосфиноксида и 2,0 г (0,111 г-моль) воды, нагревают 3 час при 100—120°С до прекращения выделения газа. Газообразные продукты реакции улавливают в системе ловушек, охлаждаемых до —70°С. Потеря в весе 6,5 г (отщепление одного C₃F₇ соответствует потере в весе 6,25 г).

Выделившийся гептафторметан идентифицируют по температуре кипения (—15°С). После охлаждения к полученной водной кислоте 15 прибавляют 7,1 г (0,06 г-моль) хлористого тионила, кипятят до прекращения выделения газа (1 час), отгоняют избыток хлористого тионила, перегоняют остаток в вакууме и получают 12,2 г (84%) бис-(перфторпропил)-20 фосфиновой кислоты, бесцветное расплывающееся на воздухе твердое вещество, т. кип. 103°С/0,95 мм; т. пл. 34—35°С.

Найдено, %: С 17,76; 17,86; Н 0,47; 0,51; Р 7,40; 7,60.



Вычислено, %: С 17,93; Н 0,25; Р 7,71.

Аналогично получают бис-(R_F-фосфиновые кислоты, перечисленные в таблице.

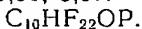
Пример 2. В круглодонную колбу на 25 мл, снабженную обратным холодильником, помещают 14,5 г (0,017 г-моль) *трис*-(перфторизомил)-фосфиноксида и 1,0 г (0,055 г-моль) воды и нагревают от 100 до 150°C в течение 3 час. Летучие продукты улавливают в системе ловушек (-70°C). После охлаждения реакционной массы неотогнанные летучие продукты отсасывают в вакууме в течение 10 мин в систему ловушек.

Потеря в весе 4,8 г (отщепление одного изо-C₅F₁₁, соответствует потере в весе 4,6 г).

Полученный изо-C₅F₁₁Н идентифицируют повторной перегонкой, т. кип. 38—41°C.

К полученной водной кислоте прибавляют 3,5 г (0,03 г-моль) хлористого тионила, кипятят до прекращения выделения газа (1 час), отгоняют избыток хлористого тионила, перегоняют остаток в вакууме и получают 8,7 г (85,0%) бис-(перфторизомил)-фосфиновой кислоты, бесцветные гигроскопичные на воздухе кристаллы, т. пл. 49—51°C.

Найдено, %: С 19,43; 19,60; Н 0,25; 0,34; Р 5,51; 5,67.



Вычислено, %: С 19,97; Н 0,17; Р 5,15. В аналогичных условиях получают бис-(R_F)-фосфиновые кислоты, указанные в той же таблице.

Номер примера	R _F	T. кип., °C/мл	T. пл., °C	Найдено, %			Брутто-формула	Вычислено, %		
				С	Н	Р		С	Н	Р
1	Перфторэтил *	60/0,40	—	15,76 15,70	0,49 0,52	9,52 9,62	C ₄ HF ₁₀ O ₂ P	15,9	0,33	10,20
1	н-Перфторбутил	110/0,40	45—47	18,04 —	0,56 0,53	6,36 6,47	C ₈ HF ₁₈ O ₂ P	19,1	0,20	6,17
2	н-Перфторамил	145/0,45	83—84	20,24 20,44	— —	5,67 5,65	C ₁₀ HF ₂₂ O ₂ P	19,97	—	5,15
2	н-Перфторгексил	140/0,20	99—100	19,25 20,26	— —	4,68 —	C ₁₂ HF ₂₆ O ₂ P	20,51	—	4,41
2	н-Перфторгептил	173/0,20	132—134	21,13 21,31	— —	4,18 4,22	C ₁₄ HF ₃₀ O ₂ P	20,95	—	3,86
2	р-Перфтороктил	192/0,20	153—154	22,03 22,00	— —	3,82 3,89	C ₁₆ HF ₃₄ O ₂ P	21,28	—	3,43

* n_D²⁰ 1,3092; d₄²⁰ 1,800; MR_D 32,25 (вычислено 32,12).

Ф о р м у л а из об р ет е н и я

Способ получения бис-(перфторалкил)-фосфиновых кислот гидролизом *трис*-(перфторалкил)-фосфиноксидов водной, отли-

20 чающимся тем, что, с целью упрощения

способа, процесс проводят при 100—150°C с последующим выделением целевого продукта при кипячении полученной смеси с хлористым тионилом.

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ELECTROCHEMICAL FLUORINATION OF TRIALKYLPHOSPHINE OXIDES

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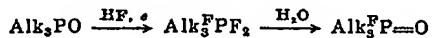
UDC 547.241.07+341.07

In the electrochemical fluorination of organic compounds containing oxygen, nitrogen, and sulfur atoms all the hydrogen atoms are replaced by fluorine with the formation of fully fluorinated compounds [1]. There are no data in the literature on the electrochemical fluorination of trialkylphosphine oxides and have shown that this results in the formation of tris(perfluoroalkyl)difluorophosphoranes, which are readily hydrolyzed, being converted into tris(perfluoroalkyl)phosphine oxides (see also [2]).

The main method by which perfluoroalkyl derivatives of phosphorus have been synthesized previously consists in the alkylation of phosphorus with perfluoroalkyl iodides. However, by this method it has only been found possible to introduce three trifluoromethyl groups on the phosphorus atom [3-5]. It has been stated [6, 7] that the introduction of three perfluoroalkyl groups, apart from CF_3 , on the phosphorus atom is impossible because of their large size. By the reaction of bis(heptafluoropropyl)iodophosphine with heptafluoropropyl iodide in presence of metallic antimony it was found possible to obtain tris(heptafluoropropyl)-phosphine [8].

Perfulorinated organophosphorus compounds, particularly those which have three perfluoroalkyl groups on the phosphorus atom, are extremely difficultly accessible. The choice of trialkylphosphine oxides as objects for the study of electrochemical fluorination is explained by their accessibility [9], the fairly high strength of the C-P bond, which is comparable with that of a carbon-carbon bond, and the considerable conductivity of their solutions in anhydrous hydrogen fluoride ($\alpha = 0.1-0.3 \Omega^{-1} \text{cm}^{-1}$, depending on the length of the alkyl group). Trialkylphosphine oxides are readily soluble in anhydrous hydrogen fluoride with the formation of homogeneous solutions containing trialkylhydroxyphosphonium salts $[\text{Alk}_3\text{P}-\text{OH}]^+\text{F}^-$ [10]. In the fluorination of these solutions the fluorination products separate in the form of a layer.

Electrochemical fluorination was carried out in a packet-type steel electrolyzer with nickel electrodes; current density 0.02-0.05 A/cm^2 , PD 5.0-6.0 V, electrolyte temperature 15-20°C. As the electrolysis process proceeded the perfulorinated products collecting on the bottom of the electrolyzer were removed in order to minimize their degradation. From the layer separated residual hydrogen fluoride was removed by the passage of air, and then the substance was rectified. As a result we obtained tris(perfluoroalkyl)phosphine oxides [2]. After a careful investigation of the fluorination products it was found that there are first formed tris(perfluoroalkyl)difluorophosphoranes, which in the removal of HF with air and distillation in glass are hydrolyzed and converted into tris(perfluoroalkyl)phosphine oxides.



It should be noted that tris(perfuloroalkyl)difluorophosphoranes and the corresponding oxides are thermally unstable: In their prolonged heating the corresponding carbenes are generated [11, 12].

In the course of electrochemical fluorination degradation processes also occur. Degradation occurs particularly strongly in the case of phosphine oxides with long-chain alkyl groups, which leads to reduction in the yields of tris(perfluoroalkyl)phosphine oxides. We were unable to obtain tris(decafluoropentyl)phosphine oxide under the above-described

*Deceased

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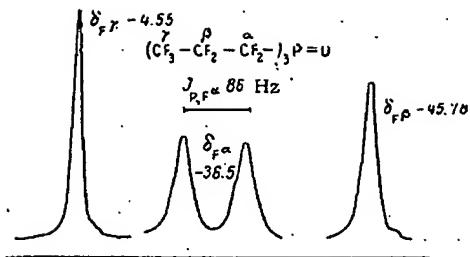


Fig. 1. ^{19}F NMR spectrum of tris(heptafluoropropyl)phosphine oxide. Chemical shifts are given relative to trifluoroacetic acid as external standard.

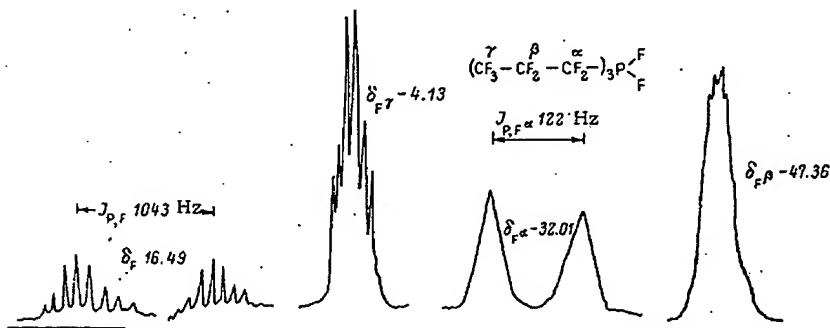


Fig. 2. ^{19}F NMR spectrum of difluorotris(heptafluoropropyl)phosphorane. Chemical shifts are given relative to trifluoroacetic acid as external standard; the signals of fluorine atoms on phosphorus are recorded relative to benzotrifluoride as external standard.

conditions. We found that the addition of bromine to the solution of the trialkylphosphine oxide in hydrogen fluoride reduces the degradation in the fluorination and makes it possible to obtain higher tris(perfluoroalkyl)phosphine oxides containing $\text{C}_5\text{-C}_8$ groups. However, the degradation of their molecules during fluorination stills occurs, and perfluoroalkanes are formed in considerable amounts. Tris(perfluoroalkyl)phosphine oxides are colorless oily liquids that can be vacuum-distilled. Their compositions and structures were confirmed by elemental analysis, NMR and IR spectroscopy, and molecular-weight determination. Physicochemical data for tris(perfluoroalkyl)phosphine oxides are given in Table 1.

In the electrochemical fluorination of tripropylphosphine oxide we isolated the initial reaction product, difluorotris(heptafluoropropyl)phosphorane. For this purpose HF was removed in a carefully dried stream of argon, and the rectification was conducted in a quartz apparatus. We then obtained a heavy colorless liquid, readily hydrolyzed by atmospheric moisture: difluorotris(heptafluoropropyl)phosphorane. In its ^{31}P NMR spectrum a triplet was observed at $\delta_p = -40.89$ ppm (in strong field relative to 85% H_3PO_4), $^1\text{J}(\text{PF}) = 1043$ Hz, while the coupling constant for interaction of phosphorus with fluorine atoms of αCF_2 fragments of perfluoroalkyl groups was $^2\text{J}(\text{PCF}_2) = 120$ Hz.

In the hydrolysis of difluorotris(heptafluoropropyl)phosphorane with the calculated amount of water in a mixture of ether and Freon 113 we obtained tris(heptafluoropropyl)-phosphine oxide. Its physicochemical data agree with those given in Table 1.

In the ^{31}P NMR spectrum of tris(heptafluoropropyl)phosphine oxide the signal from the phosphorus atom is in the region characteristic for phosphine oxides, $\delta_p = 22.36$ ppm. The constant $J(\text{PCF}_2)$ is lower than the corresponding value for difluorophosphoranes and is 85 Hz. The ^{19}F NMR spectra are given in Figs. 1 and 2.

The IR spectrum of tris(heptafluoropropyl)phosphine oxide contains a strong band at 1332 cm^{-1} characteristic for $\text{P}=\text{O}$ vibrations, and all bands at 1140 and 1220 cm^{-1} corresponding to C-F bonds.

TABLE 1. Tris(perfluoroalkyl)phosphine Oxides

Compound	Yield, %	bp, °C (p, mm)	d_4^{20}	n_D^{20}	$\nu(P=O)$, cm ⁻¹
(C ₂ F ₅) ₃ PO	23.0	98-99	1.7678	1.2906	1305
(C ₃ F ₇) ₃ PO	50.1	150-151	1.8598	1.2948	1332
(C ₄ F ₉) ₃ PO	32.4	185-187	1.8930	1.3038	1335
		82-84 (18)			
(C ₅ F ₁₁) ₃ PO	42.6	120-122 (18)	1.9052	1.3102	1354
(iso-C ₅ F ₁₁) ₃ PO	40.0	102-104 (14)	1.9050	1.3080	1354
(C ₆ F ₁₃) ₃ PO	38.0	142-144 (14)	1.9240	1.3126	1358
(C ₇ F ₁₅) ₃ PO	26.0	121-123 (0.4)	1.9450	1.3146	1360
(C ₈ F ₁₇) ₃ PO	12.3	138-140 (0.3)	1.9480	1.3184	1360

(continued)

Compound	MR _D		Found, %		Formula	Calc., %	
	found	calc.	F	P		F	P
(C ₂ F ₅) ₃ PO	40.96	40.49	69.96	7.75	C ₆ F ₁₅ PO	70.6	7.67
(C ₃ F ₇) ₃ PO	55.04	55.20	71.36	5.66	C ₆ F ₂₁ PO	72.02	5.60
(C ₄ F ₉) ₃ PO	70.34	69.97	73.00	4.38	C ₁₂ F ₂₂ PO	72.87	4.40
(C ₅ F ₁₁) ₃ PO	85.93	84.71	73.80	3.98	C ₁₈ F ₃₃ PO	73.42	3.63
(iso-C ₅ F ₁₁) ₃ PO	85.90	84.71	72.90	3.61	C ₁₈ F ₃₃ PO	73.42	3.63
(C ₆ F ₁₃) ₃ PO	101.21	99.45	73.64	3.44	C ₁₈ F ₃₉ PO	73.80	3.09
(C ₇ F ₁₅) ₃ PO	116.00	114.20	—	3.03	C ₂₁ F ₄₅ PO	—	2.69
(C ₈ F ₁₇) ₃ PO	129.10	128.94	73.82	2.68	C ₂₄ F ₅₁ PO	74.3	2.38

EXPERIMENTAL

The ³¹P NMR spectra were determined on a Bruker HX-90 pulse spectrometer at a frequency of 36.43 MHz with the use of Fourier transform. Chemical shifts were measured relative to 85% H₃PO₄ (external standard). The ¹⁹F NMR spectra were determined on a Tesla BS-487B spectrometer, working frequency 80 MHz. The IR spectra were determined on a UR-20 spectrometer. Molecular weights were determined mass-spectrometrically on an MS-902 spectrometer.

Electrochemical Fluorination of Trialkylphosphine Oxides Containing C₂-C₄ Alkyl Groups. The electrochemical fluorination of trialkylphosphine oxides was conducted in a packet-type steel electrolyzer, 1.2 liters in capacity, with nickel anodes and steel cathodes. Area of anodes 750 cm². Lining material PTFE. The initial concentration of the trialkylphosphine oxide in hydrogen fluoride was 15%, which was maintained within the range 15-20% by the periodic additions of a stock solution (an 80% solution of the trialkylphosphine oxide in hydrogen fluoride). Working conditions: current density 0.02-0.05 A/cm²; PD on electrodes 5.2-5.6 V; temperature of electrolyte 15-20°C, temperature of reflux condenser -20 to -25°C. The current was from a full-wave rectifier (made up of VSMR-200 selenium rectifiers). The electrolysis was conducted periodically (the electrolyzer was switched off overnight). As the level of the electrolyte in the electrolyzer fell, the necessary amount of hydrogen fluoride was added. The liquid perfluorinated products (the "crude" product) collected at the bottom of the electrolyzer, from which they were periodically removed. The HF dissolved in the "crude" product was removed by the passage of air, and the residue was rectified. Under the above-described conditions we carried out the electrofluorination of triethyl-, tripropyl-, and tributyl-phosphine oxides, and in yields of 15-50% we obtained the corresponding tris(perfluoroalkyl)phosphine oxides (Table 1).

Difluorotris(heptafluoropropyl)phosphorane. The fluorination of tripropylphosphine oxide was conducted in the way described above. The lower layer was removed, HF was driven out with dry argon, and the residue was left for 15 min at 20-25°C and a residual pressure of 40-50 mm. The residue remaining after the removal of HF was distilled in quartz apparatus in the vacuum of a water pump. A heavy clear liquid which fumed slightly in air came over; bp 60-62°C (24 mm). Identification was by the ³¹P and ¹⁹F NMR spectra. Found %: C 18.61; F 75.77; P 5.10. M 576. C₉F₂₃P. Calculated %: C 18.75; F 75.87; P 5.38. M 579.

Hydrolysis of Difluorotri(heptafluoropropyl)phosphorane. To a solution of 6.9 g of difluorotri(heptafluoropropyl)phosphorane in 50 ml of 1:2 mixture of ether and Freon 113

0.22 g of water was added, and the mixture was stirred for 2 h at 20°C. Solvent was driven off, the residue was distilled, and we obtained 4.1 g of a clear colorless liquid. Its physical constants were identical to those given in Table 1 for tris(heptafluoropropyl)-phosphine oxide, and the identity of the two samples was confirmed by the ^{31}P and ^{19}F NMR spectra. We also isolated 1.3 g of bis(heptafluoropropyl)phosphinic acid, which was identified by its ^{31}P NMR spectrum and physical constants, which were identical to the constants of the sample of the acid described in [6].

Electrochemical Fluorination of Trialkyphosphine Oxides Containing $\text{C}_5\text{-C}_8$ Alkyl Groups.
A 1-liter polyethylene reactor provided with a magnetic stirrer, a dropping funnel, and a reflux condenser was charged with 250 g of triisopentylphosphine and 50 g of hydrogen fluoride, and with stirring at 20°C 308 g of bromine was added in the course of 2 h. The reaction mixture was left for 1 h, cooled to 10–15°C, and added to hydrogen fluoride in the electrolyzer in an amount which gave a phosphine oxide concentration of 15–20%. The fluorination was conducted in a packet-type steel electrolyzer with a capacity of 2.4 liters; we used nickel anodes with an area of 2850 cm^2 and nickel cathodes. Conditions of process: current density 0.0245 A/cm^2 , PD on electrodes 5.9 V, temperature of electrolyte 18–20°C, temperature of reflux condenser –15 to –20°C. In the whole period of the experiment 1800 A·h of electricity was passed. We obtained 290 g of "crude" product, which after the removal of HF in a stream of air was vacuum-distilled. We obtained 245 g of tris(undecafluoro-isopentyl)phosphine oxide. A clear colorless liquid. The physical constants and analyses are given in Table 1.

Under the above-described conditions we carried out the fluorination of the oxides: $(\text{C}_5\text{H}_{11})_3\text{PO}$, $(\text{C}_6\text{H}_{13})_3\text{PO}$, $(\text{C}_7\text{H}_{15})_3\text{PO}$, and $(\text{C}_8\text{H}_{17})_3\text{PO}$.

In the fluorination of triheptyl- and trioctyl-phosphine oxides we obtained also hexadecafluoroheptane and octadecafluoroctane.

CONCLUSIONS

By the electrochemical fluorination of trialkylphosphine oxides in anhydrous hydrogen fluoride tris(perfluoroalkyl)phosphine oxides were obtained. It was shown that the initial products of the process are tris(perfluoroalkyl)difluorophosphoranes, the hydrolysis of which leads to tris(perfluoroalkyl)phosphine oxides. The structure of the compounds obtained were confirmed by methods of IR and ^{31}P and ^{19}F NMR spectroscopy.

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Izobret., Prom. Obraztsy, Tovarnye Znaki 1976, 53(1), 84. $(\text{HOSiMe}_2)_2\text{O}$ was prep'd. by hydrolysis of an equimolar mixt. of Me_2SiCl_2 with its ammonolysis products at 0-5° in a water-immiscible solvent (e.g., benzene) contg. NH_4HCO_3 .

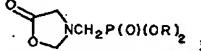
84: 105757q 1,3-Dimethyl-1,3-diphenyldisiloxane-1,3-diol. Savchenko, V. M.; Kaufman, B. L.; Karlin, A. V.; Sharkova, O. P. U.S.S.R. 497,317 (Cl. C08g), 30 Dec 1975, Appl. 2,031,180, 07 Jun 1974. From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki 1975, 52(48), 80. Title substance is obtained by hydrolysis of methylphenyldichlorosilane (I) at pH 7-9 in the presence of an acceptor of HCl. For simplifying the process and for increasing the yield of the target product, hydrolysis is carried out with the wt. ratio of I and H_2O from 1:12 to 1:20 at -10 to +20° with subsequent treatment of the hydrolyzate with a salt from a group of NaCl , NH_4Cl , for 6-72 hr.

84: 105758r Synthesis of 2-chloroalkyl phosphonic acid. Sakurai, Hiroshi; Okamoto, Yoshihige (Osaka University) Japan. 75 22,021 (Cl. C07F, B01J), 28 Jul 1975, Appl. 70 23,991, 19 Mar 1970; 2 pp. In the reaction of α -olefins with PCl_5 , PCl_3 was added and the reaction was carried out at 0-60° followed by hydrolysis of the product to give 2-chloroalkylphosphonic acids in high yields. Thus, 1-decene, PCl_5 , and C_6H_6 was heated 72 hr at room temp. to give 96% 2-chlorodecylphosphonic acid (I) and 0% 1,2-dichlorodecane (II). Without PCl_5 , 49% and 21.5% II were obtained. I is an surfactant.

84: 105759s 2-(Dialkylamino)-3-aryl-4-oxo-1,3,2-thiaaza-phospholanes. Mizrakh, L. I.; Polonskaya, L. Yu. (Institute of Biophysics, Academy of Sciences, U.S.S.R.) U.S.S.R. 491,637 (Cl. C07d), 15 Nov 1975, Appl. 2,039,256, 01 Jul 1974. From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki 1975, 52(42), 63. The title thiaazaphospholanes were prep'd. by cyclizing $(\text{R}_2\text{N})_3\text{P}$ (R = alkyl) with $\text{HSCH}_2\text{CONHR}^1$ (R^1 = aryl) at 100-30°.

84: 105760t Dialkyl α -nitroalkylphosphonates. Petrov, K. A.; Chauzov, V. A.; Bogdanov, N. N.; Pastukhova, I. V. U.S.S.R. 492,520 (Cl. C07f), 25 Nov 1975, Appl. 2,012,355, 08 Apr 1974. From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki 1975, 52(43), 64. $(\text{RO})_2\text{P}(\text{O})\text{CHR}_1\text{NO}_2$ (R = alkyl, R^1 = H, alkyl) were prep'd. by treating α -alkyl(hydro)- β -alkoxyvinylphosphonates with acetyl nitrate in Ac_2O contg. H_2SO_4 or HNO_3 .

84: 105761m Oxazolidinone phosphonates. Gaertner, Van R. (Monsanto Co.) Ger. Offen. 2,526,834 (Cl. C07F, A01N), 02 Jan 1976, US Appl. 479,932, 17 Jun 1974; 13 pp.



The cyclization of $\text{H}_2\text{NCH}_2\text{CO}_2\text{Me}$ with CH_2O and HP(O)(OR)_2 gave I (R = Et, allyl, Me, Bu, Me_2CH , MeCHClCH_2), which were useful as herbicides.

84: 105762n Substituted pyridine phosphonothioates.

Pawloski, Chester E. (Dow Chemical Co.) U.S. 3,927,004 (Cl. 260-294.8K; C07D), 16 Dec 1975, Appl. 457,023, 01 Apr 1974; 4 pp. The reaction of PhP(S)(OMe)Cl with pyridinols gave PhP(S)(OMe)OR (R = 3,5-dichloro-6-propoxy-2-pyridinyl, 2,4,6-trichloro-2-pyridinyl, 5-methyl-2-pyridinyl, 6-methoxy-2-methyl-3-pyridinyl, 5-chloro-3-methyl-2-pyridinyl, 6-methyl-1-3-pyridinyl, and 6-chloro-2-pyridinyl). Data was given for use of the pyridine phosphonothioates as insecticides.

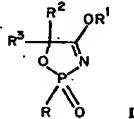
84: 105763p N-Phosphonomethyl glycine. Gaertner, Van R. (Monsanto Co.) U.S. 3,927,080 (Cl. 260-502.5; C07F), 16 Dec 1975, Appl. 502,706, 03 Sep 1974; 3 pp. $(\text{HO})_2\text{P}(\text{O})\text{CH}_2\text{NHCH}_2\text{CO}_2\text{Et}$ (I) was produced by the acid hydrolysis of $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{N}(\text{CM}=\text{E})\text{CH}_2\text{CO}_2\text{Et}$ (II). I was useful as a post-emergent broad spectrum herbicide (no data). Thus, 0.1 mole of $\text{BrCH}_2\text{CO}_2\text{Et}$ was added to 0.3 mole Me_3CNH_2 to give 58% $\text{Me}_3\text{NHCH}_2\text{CO}_2\text{Et}$, which was treated formalin, using 0.1 mole of H_2CO equiv. for 0.1 mole of amino group content, and with 0.11 mole of $(\text{EtO})_2\text{POH}$ to give II. II was hydrolyzed with 48% aq. HBr to give 95% I.

84: 105764q Phenylthiophosphonyl dichloride. Ura, Yasukazu; Takamatsu, Hideki. (Nissan Chemical Industries, Ltd.) Ger. Offen. 2,527,650 (Cl. C07F), 08 Jan 1976, Japan. Appl. 74 71,616, 22 Jun 1974; 16 pp. The prepn. of PhP(S)Cl_2 from benzene and Cl_3PS in an autoclave at 100-300° was catalyzed by Al, AlCl_3 , $\text{AlCl}_3\text{-PCl}_3$, $\text{AlCl}_3\text{-P}_2\text{S}_5$, and $\text{AlCl}_3\text{-P}_2\text{S}_5\text{-PCl}_3$. Thus, 0.25 mole Cl_3PS , 0.25 mole benzene, and 0.5 g Al at 180° 4 hr in a 100 ml autoclave gave 75% PhP(S)Cl_2 .

84: 105765r Selective extraction of triphenylphosphine oxide. Tampieri, Maurizio; Gregorio, Guglielmo; Andreotti, Alberto (Montedison S.p.A.) Ger. Offen. 2,526,129 (Cl. C07F), 02 Jan 1976, Ital. Appl. 23850/74, 11 Jun 1974; 15 pp. The reaction mixt. of the hydroformylation of propylene contg. 65% Ph_3P and Rh- Ph_3P complex, 15% aldol condensation product and 20% Ph_3PO was treated with aq. MeOH , which reduced the content of Ph_3PO by 45%. Treatment with aq. Me_2CO reduced the content of Ph_3PO by 20%.

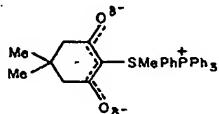
84: 105766s 2-Oxo-2-alkyl-4-alkoxy-1,3,2-oxazaphospholines. No, B. I.; Shishkin, V. E.; Yukhno, Yu. M. (Volgograd Polytechnic Institute) U.S.S.R. 498,313 (Cl. C07f), 05 Jan

1976, Appl. 2,032,093, 13 Jun 1974. From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki 1976, 53(1), 85. Title compds.



I (R, R^1 = alkyl; R^2 , R^3 = H, alkyl) were prep'd. by treating an α -hydroxyimino carboxylic acid or ester with an equimolar amt. of RP(O)Cl_2 in an org. solvent (e.g., dioxane) contg. an HCl acceptor (e.g., Et_3N) at 10-20°.

84: 105767t 2-(Methylphenyl(triphenylphosphonio)sulfuryl)-5,5-dimethyl-1,3-cyclohexanedione. Arbusov, B. A.; Belkin, Yu. V. (Kazan State University) U.S.S.R. 498,312 (Cl. C07F), 05 Jan 1976, Appl. 2,030,380, 07 Jun 1974. From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki 1976, 53(1), 85. The title compd. (I) was prep'd.



84: 105768u Bis (perfluoroalkyl)phosphinic acids. Semenii, V. Ya.; Zavatskii, V. N.; Liptuga, N. I.; Yagupolskii, L. M. (Institute of Organic Chemistry, Academy of Sciences, Ukrainianian S.S.R.) U.S.S.R. 498,311 (Cl. C07F), 05 Jan 1976, Appl. 1,883,723, 16 Feb 1973. From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki 1976, 53(1), 85. $\text{R}_2\text{P(O)OH}$ (R = perfluoroalkyl) were prep'd. by partial hydrolysis of R_3PO with H_2O at 100-50°, followed by treatment with refluxing SOCl_2 .

84: 105769v Dialkylamido esters of alkoxy methyl phosphonic acids. Krutskii, L. N.; Krutskaya, L. V.; Simonenko, A. A. (Kuzbas Polytechnic Institute) U.S.S.R. 498,310 (Cl. C07f), 05 Jan 1976, Appl. 1,949,429, 17 Jul 1973. From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki 1976, 53(1), 85. Title compds. were prep'd. by treating tetraalkyl diamido dichlorophosphites with a halomethyl alkyl ether and then with a 2-fold excess of alc.

84: 105770p (Alkoxy methyl) thiophosphonic acid tetraalkyl-diamides. Krutskii, L. N.; Krutskaya, L. V.; Simonenko, A. A. (Kuzbas Polytechnic Institute) U.S.S.R. 498,309 (Cl. C07F), 05 Jan 1976, Appl. 1,949,429, 17 Jul 1974. From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki 1976, 53(1), 84-5. Title compds. were prep'd. by treating tetraalkyl diamido dichlorophosphites with halomethyl alkyl ethers and then H_2S at 50-60° in an inert org. solvent contg. 2 equiv org. base.

84: 105771q Purification of technical chlorophos. Vershinin, P. V.; Komova, S. N.; Golovtsov, I. N.; Shvetsova-Shilovskaya, K. D. U.S.S.R. 498,308 (Cl. C07F), 05 Jan 1976, Appl. 2,029,374, 03 Jun 1974. From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki 1976, 53(1), 84. Purifn. of tech. chlorophos by treatment with an alk. agent in an org. solvent was improved by using anhyd. NH_3 or Na_2CO_3 at pH 4-7, followed by treatment with ethylene oxide.

84: 105772r Dialkyl tin dichlorides. Umeno, Masayuki; Abe, Fujio; Uchida, Junzo; Konami, Tomiyoshi (Hokko Chemical Industry Co., Ltd.) Japan. 75 24,950 (Cl. C07F, B01J), 20 Aug 1975, Appl. 69 104,353, 26 Dec 1969; 3 pp. Treating tetra(higher alkyl) stannanes with SnCl_4 in the presence of 1-20 wt. % activated clay, at 170-230° gave di(higer alkyl)tin dichlorides. Thus, tetra-n-octylstannane was heated with SnCl_4 and activated clay to give 97.5% product, contg. 96.3% di-n-octyltin dichloride.

84: 105773s Recovering solubilized organotin halides. Larkin, William A.; Bouchoux, Jean W. (M and T Chemicals Inc.) U.S. 3,931,264 (Cl. 260-429.7; C07F), 06 Jan 1976, Appl. 499,503, 22 Aug 1974; 4 pp. Organotin halides can be recovered quant. from their aq. solns. by adding a non-reactive highly sol. inorg. salt to partially or completely saturate the soln. and then heating the resultant soln. to sep. the organotin halide from the aq. phase. The solv. of the organotin halides in water at 21° and 100° was given in addn. to the grams of CaCl_2 added to the aq. organotin halide solns. at 21°, 70°, and 100°. The organotin halides tested were: Me_3SnCl , Me_2SnCl_2 , Me_3SnCl , Et_3SnCl , Et_2SnBr_2 , Bu_2SnCl_2 , Ph_2SnCl_2 , $\text{Me}(\text{CH}_2)_7\text{SnCl}_2$, and Bu_2SnCl_2 .

84: 105774t Manganese cyclopentadienide and its alkyl derivatives. Tsursumiya, G. S.; Agladze, T. R.; Kolotyrkin, Ya. M.; Shapiro, I. O. U.S.S.R. 498,314 (Cl. C07F), 05 Jan 1976, Appl. 1,959,963, 09 Aug 1973. From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki 1976, 53(1), 85. Title compds. prep'n. by electrolysis of a cyclopentadienyl metal or its alkyl deriv. (using a Mn anode and Cu or Pt as the cathode) was improved by using cyclopentadienylthallium or its alkyl deriv. at 10-15 V in Me_2SO contg. LiCl or LiClO_4 .